Table I. C–C Distances within the Ortho-Dimetalated Ring

Bond	Bond length, Å	
	Molecule A	Molecule B
C(18)–C(13)	1.424 (8)	1.437 (9)
C(13)–C(14)	1.427 (8)	1.432 (8)
C(14)–C(15)	1.364 (9)	1.373 (10)
C(15)–C(16)	1.381 (10)	1.390 (10)
C(16)–C(17)	1.362 (9)	1.365 (9)
C(17)–C(18)	1.446 (8)	1.448 (9)

in parentheses immediately following the entry for molecule A.)

The molecule contains an $(OC)_3Fe-Fe(CO)_3$ unit, in which the Fe–Fe distance is 2.471 (1) Å (2.466 (1) Å), which is doubly bridged by a $C(CHO)P(Ph_2C_6H_4)$ ligand bonding from the original ylide carbon atom (labeled "C" in Figure 1) and the ortho-carbon atom of one phenyl ring (designated C(18)). The angle between the Fe(1)–C–Fe(2) and Fe(1)–C(18)–Fe(2) planes is 106.70° (106.45°). The $C(CHO)P(Ph_2C_6H_4)$ ligand is formally derived by attack of a carbonyl fragment at the ylide carbon atom, followed by (or in concert with) transfer of an ortho hydrogen from the PPh_3 moiety.

In valence bond terms, the phosphorus atom is best thought of as the center for a phosphonium cation. Thus, P–Ph distances average 1.803 Å, the P–C(13) distance is 1.785 (6) Å (1.784 (6) Å), and the P–C (ylide) distance is 1.748 (6) Å (1.749 (6) Å). The formal positive charge on the phosphorus atom is counterbalanced by a negative charge delocalized over the C(13)–C(14)–C(15)–C(16)–C(17) system; the conjugation around the six-membered ring is broken by dimetallation of the ortho position (C(18)), making this ring approximate that of a Meisenheimer complex found in nucleophilic aromatic substitution reactions. In keeping with this view, the ortho-dimetalated phenyl ring is only slightly distorted from planarity, with C(18) being displaced some 0.031 (6) Å (0.037 (6) Å) from the plane defined (root mean square deviation 0.004 Å) by atoms C(13) through C(17). In addition to this, the internal angle at C(18) is reduced toward the regular tetrahedral angle, having a value of 114.3 (5)° (113.4 (5)°). Distances within this system are listed in Table I.

The Fe(1)–C(18)–Fe(2) bridge is rather asymmetric, the Fe(1)–C(18) distance being 2.001 (6) Å (1.986 (6) Å), i.e., some 0.15–0.20 Å shorter than the Fe(2)–C(18) bond length of 2.159 (5) Å (2.185 (6) Å). The Fe(1)–C(18)–Fe(2) angle is 72.76 (19)° (72.29 (20)°). In contrast to this, the Fe(1)–C(ylide)–Fe(2) bridge is fairly regular, with Fe(1)–C(ylide) 2.037 (6) Å (2.036 (6) Å), Fe(2)–C(ylide) 2.047 (6) Å (2.052 (6) Å), and ∠Fe(1)–C–Fe(2) 74.44 (19)° (74.19 (20)°). The aldehydic function is normal with C(ylide)–C(A) 1.448 (8) Å (1.453 (9) Å), C(A)–O(A) 1.218 (9) Å (1.220 (9) Å), and ∠C–C(A)–O(A) 125.8 (6)° (124.5 (6)°).

Finally, it should be noted that, despite the steric availability of a third bridging site between the metal atoms, there is no bridging hydride ligand. This has been confirmed by detailed difference-Fourier syntheses in addition to the mass spectrometric and ^1H NMR results reported above.

Acknowledgment. This work has been generously supported by the National Science Foundation through Grant CHE77-04981 (to M.R.C.)

Supplementary Material Available: Tables of x-ray crystallographic data (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) E. W. Abel, *Ann. N.Y. Acad. Sci.*, **239**, 306 (1974).
(2) E. W. Abel, C. A. Burton, M. R. Churchill, and K. G. Lin, *J. Chem. Soc., Chem. Commun.*, 269 (1974); M. R. Churchill and K. G. Lin, *Inorg. Chem.*, **14**, 1133 (1975).
(3) E. W. Abel, C. A. Burton, M. R. Churchill, and K. G. Lin, *J. Chem. Soc., Chem. Commun.*, 917 (1974); M. R. Churchill and K. G. Lin., *Inorg. Chem.*, **14**, 1675 (1975).
(4) M. R. Churchill, B. G. DeBoer, F. J. Rotella, E. W. Abel, and R. J. Rowley, *J. Am. Chem. Soc.*, **97**, 7158 (1975).
(5) H. Schmidbauer and W. Tronich, *Chem. Ber.*, **100**, 1032 (1967).
(6) Y. Ishii, personal communication.
(7) Anal. Calcd: C, 53.65; H, 2.60. Found: C, 53.20; H, 2.46.
(8) The experimental method has been described previously. See M. R. Churchill, R. A. Lashewycz, and F. J. Rotella, *Inorg. Chem.*, **16**, 265 (1977).

Melvyn Rowen Churchill,* Frank J. Rotella
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Edward W. Abel,* Stuart A. Mucklejohn
Department of Chemistry, University of Exeter
Exeter EX4 4QD, England

Received May 10, 1977

The Relationship between Substituent Effects on Energy and on Charge from ab Initio Molecular Orbital Theory[1]

Sir:

Ab initio molecular orbital calculations at the minimal basis set STO-3G level have proven successful in reproducing the experimental gas phase energies (relative proton affinities) for a variety of *isodesmic* proton transfer equilibria.[2-5] With substituted methylamines,[2] for example,

$$XCH_2NH_3^+ + HCH_2NH_2 \rightleftharpoons XCH_2NH_2 + HCH_2NH_3^+ \quad (\Delta E^\circ_{\text{calcd}} \simeq \Delta H^\circ_{\text{obsd}}) \qquad (1)$$

Ab initio calculations of charge densities have been shown also to successfully correlate ^{13}C NMR shifts[6] and infrared intensities[7] in monosubstituted benzenes. We wish now to report the preliminary findings from this theory regarding substituent effects on the protonic charge of the cation and the corresponding energy charge for proton transfer. This is a matter of substantial importance since many of the concepts of organic chemistry are described in terms of the charge-releasing or -donating properties of substituents. Included are the σ-inductive effect, π-inductive effects, and resonance interactions.[7] Only the field effect, the electrostatic interaction of a substituent dipole with a distant dipolar or charge reaction site, is expressed in energy terms. While some properties such as NMR chemical shifts are often thought of as dependent on charge,[8] the vast majority of substituent effect correlations (e.g., of equilibria and reaction rates) involve energy, not charge measurements.

Implicit in the interpretation of fundamental energy changes in terms of the movement of charge is the assumption that the two quantities are directly related to one another. This assumption was specifically incorporated into the early theoretical treatment of aromatic acid dissociation energies by Roberts and Jaffe.[9] Much more recently, an empirical model of proton affinities has been postulated which assumes a direct relationship between this parameter and hydrogen charge density.[10] However, surprisingly little direct evidence is available on this point. Calculations at the INDO level have shown[11] that the charge on the carboxylic acid hydrogen atom in substituted benzoic acids is approximately proportional to the pK_a values expressed as Hammett σ constants. Ab initio molecular orbital calculations at the STO-3G level have shown that the nitrogen inversion barrier in substituted anilines[12] and the torsional barriers in para-substituted phenols,[13] respectively, parallel the extent of π charge transfer between the ring and the NH_2 and OH groups. Rotational barriers in mono-

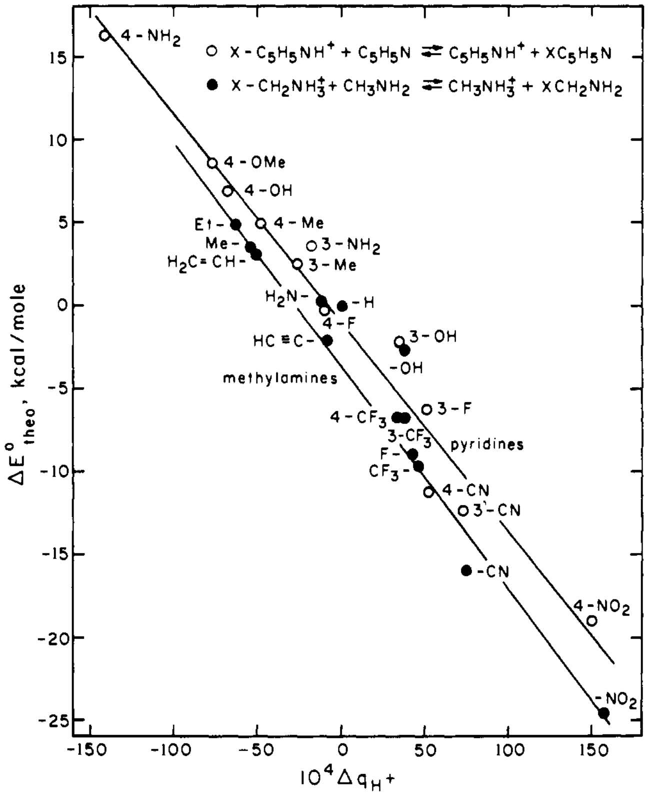

Figure 1. Ordinate: ΔE°_{theo} for proton transfer reaction. Abscissa: 10^4 Δq_H of protonated form. Open circles for 3- and 4-substituted pyridinium ions. Closed circles for substituted methyl ammonium ions. Substituent, X, is indicated. Upper slope is 1263 kcal/e (SD = 1.9 kcal; R = 0.982) and lower slope is 1354 kcal/e (SD = 2.4 kcal; R = 0.969).

substituted benzenes are proportional to the charge-dependent intensities of certain infrared bands in the same molecules.[14] By contrast, the total charge densities at the central carbon atoms in methyl, ethyl, isopropyl, and *tert*-butyl cations become increasingly positive[15] in this sequence, in reverse to the order of decreasing stability (increasing hydride affinity). Similar reverse effects have been observed in other systems.[16]

For substituted methyl- and ethylammonium,[2] -quinuclidinium,[3] -pyridinium,[4] and -anilinium[4] ions the *isodesmic* proton transfer reactions, e.g., 1, are found by the STO-3G minimal basis set calculations[17] to give ΔE° values which are linearly related to the corresponding Mulliken charge of the acidic proton of the substituted ion relative to the unsubstituted one, e.g., $\Delta q_H = q(XCH_2NH_3^+) - q(HCH_2NH_3^+)$. Figure 1 depicts the charge-energy relationship for substituted methylammonium and for 3- and 4-substituted pyridinium ions. The Δq_H values in the former case are averages for the three protons relative to the average in the unsubstituted compound. Linear correlations have also been obtained in the other cases. Both 3 and 4 substituents are accommodated on a single regression line for both the pyridines and the anilines.

The slopes of the lines in kcal mol^{-1} per electron are remarkably similar: substituted methylammonium ions, 1350; substituted ethylammonium ions, 2100 (trans proton alone, 1350); 4-substituted quinuclidinium ions, 2250; 3- and 4-substituted pyridinium ions, 1263; meta- and para-substituted anilinium ions, 1900. Linear correlations also exist for proton transfer energies vs. total charge on the NH_2^+ group, although they show somewhat more scatter. Interestingly enough, the average charge on the hydrogen atoms in the neutral bases also correlates with the corresponding ΔE° values. Such a plot for substituted methylamines has a slope of 2250. In addition, calculations for 3- and 4-substituted pyridinium ions which are hydrogen-bonded to a single water molecule also show a linear relationship between ΔE° and Δq_H.[18] Since ΔE° in this case includes substituent-induced changes in hydration energy, this observation suggests that solvation energy depends upon the charge density at the site of solvation. This is a significant observation since it helps to rationalize the existence of linear free-energy relationships in solution.

A series of 4-substituted benzoic acids also shows a linear relationship for ΔE° vs. Δq_H with a slope of 1800 kcal mol^{-1}/e.[5] Similar correlations exist for the Δq_{OH} and Δq_{O^-} terms. In addition, separation of substituent effects upon ΔE° into field and resonance components indicates that these parameters independently demonstrate linear energy-charge density correlations. In the case of the resonance component, the charge density parameter is the total change in π-electron density in neutral benzoic acid.[5] Our initial investigations with analogous reactions for substituted phenols indicate similar correlations to those discussed above. Thus the theoretical calculations show approximately linear charge-energy relationships for substituent effects on proton transfer from a wide variety of acidic centers. However, in the acidities of toluenes and benzenes, two distinct linear relationships appear—one for electron-withdrawing substituents and a second of much steeper slope ($\delta E/\delta \Delta q_H$) for π-electron donor substitutents. Work is in progress to further define the limitations as well as the theoretical basis, for these interesting charge-energy relationships.

References and Notes

(1) This work was supported in part by grants from the National Science Foundation and the Public Health Service (R.W.T.) and the National Research Council of Canada (W.F.R.).
(2) M. Taagepera, W. J. Hehre, R. D. Topsom, and R. W. Taft, *J. Am. Chem. Soc.*, **98,** 7438 (1967).
(3) M. Taagepera, R. W. Taft, W. J. Hehre, and C. A. Grob, unpublished results.
(4) Unpublished results of W. J. Hehre cited in R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975, p 31.
(5) P. G. Mezey and W. F. Reynolds, *Can. J. Chem.*, in press.
(6) W. J. Hehre, R. W. Taft, and R. D. Topsom, *Progr. Phys. Org. Chem.*, **12,** 159 (1976).
(7) For a recent review, see R. D. Topsom, *Progr. Phys. Org. Chem.*, **12,** 1 (1976).
(8) Strictly speaking, however, NMR chemical shift-σ-parameter correlations, or any other kind of frequency-log K correlations are energy-energy relationships.
(9) J. L. Roberts and H. H. Jaffe, *Tetrahedron, Suppl.* 2, 19 455 (1963).
(10) D. W. Davis and D. A. Shirley, *J. Am. Chem. Soc.*, **98,** 7898 (1976).
(11) S. Kang and D. L. Beveridge, *Theor. Chim. Acta*, **22,** 312 (1971); S. Kang and M. H. Cho, *Int. J. Quantum Chem.*, Sym. No. 7, 319 (1973).
(12) W. J. Hehre, L. Radom, and J. A. Pople, *J. Chem. Soc., Chem. Commun.*, 669 (1972).
(13) L. Radom, W. J. Hehre, J. A. Pople, G. L. Carlson, and W. G. Fately, *J. Chem. Soc., Chem. Commun.*, 308 (1972).
(14) T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 287 (1974).
(15) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94,** 5935 (1972).
(16) See, for example, J. F. Wolf, P. G. Harch, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **97,** 2902 (1975).
(17) All calculations have been carried out at the STO-3G level (W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51,** 2659 (1969)) using the gaussian-70 series of computer programs (Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.). Charges have been calculated via the Mulliken approximation: R. S. Mulliken, *J. Chem. Phys.*, 1833, 1841, 2338 2343 (1955).
(18) E. M. Arnett, B. Chawla, L. Bell, M. Taagepera, W. J. Hehre, and R. W. Taft, *J. Am. Chem. Soc.*, submitted for publication.
(19) Alfred P. Sloan Fellow, 1974–1976.
(20) Department of Organic Chemistry, La Trobe University, Bundoora, Victoria, Australia.

W. F. Reynolds, P. G. Mezey
Lash Miller Chemical Laboratories
University of Toronto, Toronto, Canada M5S 1A1

W. J. Hehre,[19] R. D. Topsom,[20] R. W. Taft*
Department of Chemistry, University of California, Irvine
Irvine, California 92717

Received March 7, 1977